High-spin Nickel(II) Complexes of Penta-aza Macrocycles: Characterization, Electronic Spectra, and Thermodynamic Properties

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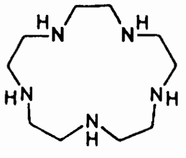
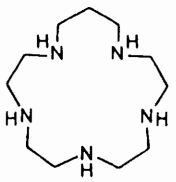
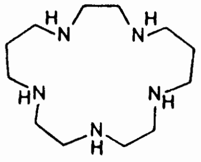
High-spin nickel(II) complexes of 15-, 16-, and 17-membered saturated penta-aza macrocycles [1,4,7,10,13-penta-azacyclopentadecane (L^1); 1,4,7,10,13-penta-azacyclohexadecane (L^2); and 1,4,7,11,14-penta-azacycloheptadecane (L^3)] have been synthesized and characterized. Their electronic spectra, magnetic moments, and heats of formation are reported. The complexes appear to form distorted octahedra in solution, with the macrocycles folded. In the complexes of L^2 and L^3 one six-membered ring apparently lies in the equatorial plane of the molecule. The heats of formation lie in the sequence $L^1 < L^3 < L^2$. These complexes do not exhibit a positive macrocyclic enthalpy effect.

Triaza- and especially tetra-aza macrocycles have been the subject of many studies [1] because of the unusual properties frequently conferred upon the metal atom when bound to such macrocycles. Several studies of penta-aza macrocycles containing a pyridine ring have appeared,[2-5] including some *X*-ray analyses which show that the macrocyclic ring is folded.[6] Recently, Kodama and Kimura [7] reported the synthesis of a series of saturated penta-aza macrocycles, L^1—L^3, and studied their complex formation with copper(II).


L^1


L^2


L^3

In view of our interest in the spectroscopic and thermodynamic properties of macrocycles, we have synthesized nickel(II) complexes of L^1—L^3 with a view to studying their thermodynamic and spectroscopic properties and to see whether they behave in a manner similar to those with tetra-aza macrocycles, with respect to the formation of high-spin (blue) and low-spin (yellow) complexes.[8-10] We were also interested to learn whether the enhancement of exothermicity, observed in the complexes of the tetra-aza macrocycles when five- and six-membered rings alternated, would also be observed in the penta-aza series.

EXPERIMENTAL

Ligands L^1—L^3 were prepared by a route involving condensation of the appropriate tosylated segments, followed by hydrolysis of the pentatosylated derivatives and extraction of the ligand, according to the procedure described by Smith *et al.*[11]

Nickel(II) complexes of L^1 and L^2 were prepared by mixing hot ethanol solutions (*ca.* 0.2 mol dm^{-3}) of ligand and $Ni[ClO_4]_2 \cdot 6H_2O$ in equimolar amounts, and refluxing the mixture for *ca.* 1 h. The pale violet complexes precipitated on cooling and were collected by filtration under nitrogen.

The nickel(II) complex of L^3 was prepared in a similar way, but required higher dilution (*ca.* 0.04 mol dm^{-3} solutions of metal and ligand) and reflux of the dark yellow mixture for 2 d. The mixture became violet, while a pale pink-violet precipitate formed. This precipitate was collected by filtration under nitrogen and stored in a vacuum desiccator {Found: C, 25.4; H, 5.3; N, 14.8%; $\mu_{eff.}$ = 1.33 B.M. at 298 K. Calc. for $[NiL^1][ClO_4]_2$: C, 25.5; H, 5.5; N, 14.8%. Found: C, 26.8; H, 5.3; N, 14.6%; $\mu_{eff.}$ = 3.01 B.M. at 298 K. Calc. for $[NiL^2][ClO_4]_2$: C, 26.9; H, 5.6; N, 14.4%. Found: C, 28.7; H, 5.9; N, 14.2%; $\mu_{eff.}$ = 3.39 B.M. at 298 K. Calc. for $[NiL^3][ClO_4]_2$: C, 28.8; H, 5.8; N, 14.0%}.†

Calorimetric apparatus and procedures and reagents for thermodynamic measurements have already been described.[12] Visible spectra were recorded on a Beckman DK 2A spectrophotometer, u.v. spectra with a Varian Cary 17 spectrophotometer. They are reported in Figure 1. Magnetic data were obtained by the Faraday method using a Sartorious balance.

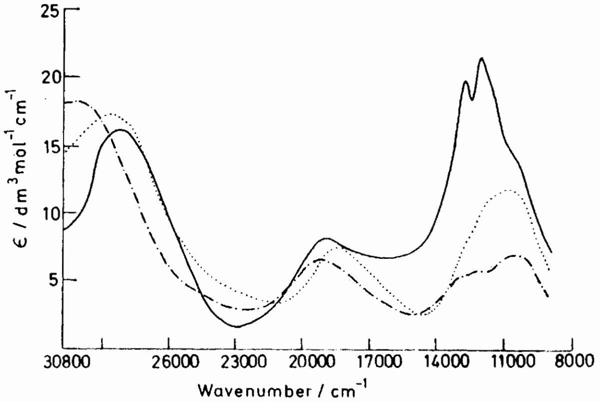


Figure 1 Electronic spectra of the nickel(II) complexes of L^1 (——), L^2 (— · —), and L^3 (· · ·)

DISCUSSION

In Tables 1—3 we report the thermodynamic and spectroscopic properties of the nickel(II) complexes of these three penta-aza macrocycles, L^1—L^3.

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 cal = 4.184 J.

Of primary importance is a clear appreciation of the structures of these species in solution. Ligands similar to macrocycles L^1—L^3 are known to form seven-co-ordinate pentagonal-bipyramidal complexes with iron(III) and manganese(II).[5,13] Moreover, seven-co-ordinate nickel(II) is also known with an open-chain ligand.[14] Although there is the possibility that the present species are also seven-co-ordinate in solution, involving a pentagonal bipyramid with five nitrogen atoms in the equatorial plane or a capped-octahedral structure, we consider this unlikely for a variety of reasons.

TABLE 1

Heats of formation of high-spin nickel(II) complexes with penta-aza macrocycles and related systems

L	$-\Delta H^{\ominus}$/ kcal mol^{-1} [a]	Ref.
L^1	16.1(2)	*b*
L^2	23.0(2)	*b*
L^3	19.4(2)	*b*
L^6 (2,2,2,2) [c]	11.9	12
L^4 (2,2,2,3)	20.0	12
L^5 (2,3,2,3)	24.1	*d*
L^7 (2,2,2,4) [e]	12.8	21
$H_2N[CH_2]_2NH[CH_2]_2NH[CH_2]_2NH_2$	14.0	*f*
$H_2N[CH_2]_2NH[CH_2]_3NH[CH_2]_2NH_2$	19.2	*d*
$H_2N[CH_2]_3NH[CH_2]_2NH[CH_2]_3NH_2$	19.5 [g]	20
tetren	18.9	15

[a] Values in parentheses are standard deviations in the last significant figure. [b] This work. [c] 1,4,7,10-Tetra-azacyclododecane. [d] L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, 1978, **17**, 1042. [e] 1,4,7,10-Tetra-azacyclotetradecane. [f] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115. [g] Obtained from ref. 20 and corrected for the yellow-to-blue conversion (ref. 8).

TABLE 2

Observed and calculated electronic spectra (cm^{-1}) [a] in aqueous solution

	$[NiL^1]^{2+}$			
	10 520 (sh), 12 077(21), 12 770(20), 19 010(8), 28 570(16)			
	$[NiL^2]^{2+}$		$[NiL^3]^{2+}$	
Assignment [b]	Obs.	Calc.[c]	Obs.	Calc.[c]
$^3E_g{}^a$	10 420(7)	10 525	10 930(12)	10 840
$^3B_{1g}$, $^1A_{1g}$	12 250(5.9)	12 900	12 077 (sh)	12 770
	12 900(5.4)		12 770 (sh) (8.2)	
$^3A_{2g}{}^a$	*ca.* 17 000	17 220	*ca.* 17 000	17 100
$^3E_g{}^b$	19 230(6.7)	19 090	18 450(7.7)	18 605
$^3A_{2g}{}^a$		29 700		28 250
$^3E_g{}^c$	30 525(19.9)	30 555	28 820(19)	28 760

[a] Absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] See ref. 26; superscripts a, b, c indicate order of states. [c] Using parameters shown in Table 3.

Penta-aza macrocycles similar to these, but containing a pyridine ring, have been studied previously[4] and are expected to occupy five positions of a five- or six-co-ordinate structure through appropriate folding of the macrocyclic ring. This has been proven by *X*-ray analyses of copper(II) and cobalt(III) complexes of one of these penta-aza macrocycles. The former complex is trigonal bipyramidal and the latter octahedral.[6] Copper complexes of the macrocycles L^1—L^3 have been reported and presumed to be folded.[7]

The open-chain ligand 3,6,9-triazaundecane-1,11-diamine (tetren)[15] forms a six-co-ordinate complex with nickel(II) whose electronic spectrum is very similar to those of the nickel complexes of L^2 and L^3. As we discuss below, these spectra are consistent with a distorted octahedron.

Seven-co-ordinate complexes of manganese(II) are known in solution.[16-18] The $\Delta H^{\ominus}$ values in such cases, for example with penten [*NNN'N'*-tetrakis(2-aminoethyl)ethane-1,2-diamine], are anomalously high when compared with analogous six-co-ordinate species.[19]

In contrast as we discuss below, the nickel complexes of the penta-aza macrocycles do not exhibit $\Delta H^{\ominus}$ values greater than the six-co-ordinate analogues. Attempts to protonate these nickel complexes were unsuccessful, from which we may conclude that all five nitrogen atoms are co-ordinated to nickel. Since the electronic spectra, discussed below, are inconsistent with five- or seven-co-ordination (high spin) we conclude that these complexes possess a distorted octahedral structure with four nitrogen atoms bound in the plane and the macrocycle folded so as to provide a fifth amine nitrogen above the plane. The sixth site is occupied by a water molecule. Further evidence for this type of structure is derived from the observation that no yellow low-spin four-co-ordinate nickel(II) complexes can be detected (even at high ionic strength) in solution, in equilibrium with the octahedral species. These would be expected, by analogy with the tetra-aza series,[8-10] if one nitrogen atom remains unco-ordinated.

Since the macrocycle L^1 contains five-membered rings and five equivalent nitrogen atoms there is no ambiguity concerning the gross structure of its nickel complex. However, with the macrocycle L^2 containing one six-

TABLE 3

Calculated parameter sets (cm^{-1}) [a] for some macrocyclic nickel(II) complexes

Ligand	*DQ*	*DS*	*DT*	*B*	DQ_A	DQ_E	σ_N	σ_Z	π_Z	Ref.
L^2	31 464	−3 732	−3 385	952	23 453	35 469	4 000	2 609	−175	*b*
L^3	31 801	−2 595	−2 798	794	25 179	35 111	4 256	2 999	−40	*b*
L^5	30 604	−6 867	−8 527	831	10 425	40 693	4 933	1 398	101	25
L^8 [c]	28 166	−5 845	−5 057	825	16 198	34 149	4 140	1 537	−320	25
L^9 [d]	25 119	−4 641	−4 704	834	13 987	30 684	3 719	1 526	−127	25

[a] The penta-aza macrocycle complexes were examined in aqueous solution; the axial field comprises one nitrogen atom of the macrocycle and one water molecule. The reference tetra-aza macrocycle complexes were examined as chloride salts in the solid state;[25] the axial ligands are two chloride ions. The basic data set comprises *DQ*, *DS*, *DT*, and *B*. The normalized spherical harmonic (NSH) formalism and orbital angular-overlap model are used (ref. 26; J. C. Donini, B. R. Hollebone, and A. B. P. Lever, *Prog. Inorg. Chem.*, 1977, **22**, 225; J. Glerup, O. Monsted, and C. E. Schäffer, *Inorg. Chem.*, 1976, **15**, 1399). [b] This work. [c] 1,4,8,12-Tetra-azacyclopentadecane. [d] 1,5,9,13-Tetra-azacyclohexadecane.

membered ring, ambiguity exists (see Figure 2). Previously we have observed that replacement of a five with a six-membered ring, to generate alternating ring sizes in a polyamine ligand, increases the enthalpy of formation of the metal complex.[20] The considerable increase in heat of formation of $[NiL^2]^{2+}$ compared to $[NiL^1]^{2+}$, namely 7 kcal mol^{-1}, may be compared with an increase of 6.2 kcal mol^{-1} in passing from the planar low-spin nickel complexes of 1,4,7,10-tetra-azacyclotridecane (L^4) to 1,4,8,11-tetra-azacyclotetradecane (L^5) [12] or 6.1 kcal mol^{-1} in passing from *trans*-diaqua(3,6-diazaoctane-1,8-diamine)copper(II) to (3,7-diazanonane-1,9-diamine)-copper(II). In the complexes taken as references, the ligand has been assumed to have an in-plane disposition. It is likely, therefore, that the six-membered ring in L^2 is found in the equatorial plane of the distorted octahedron. The apical rings are then five-membered [see Figure 2, (A) and (B)].

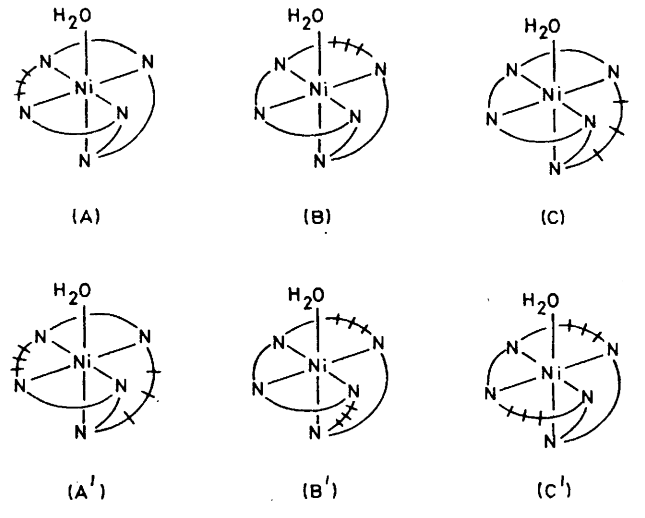

Figure 2 Possible isomers of the complexes $[NiL^2]^{2+}$ (A, B, C) and $[NiL^3]^{2+}$ (A′, B′, C′). Six-membered rings are indicated by three bars, whilst five-membered rings have none. The balance of evidence favours isomers (A) or (B) in each case

With $[NiL^3]^{2+}$ there is a reduction in $-\Delta H^\ominus$ relative to $[NiL^2]^{2+}$. If both six-membered rings, which alternate, are found in the plane, we could expect a further large increase in $-\Delta H^\ominus$ (*e.g.* compare $[NiL^4]^{2+}$ with $[NiL^5]^{2+}$).[12] It is probable, therefore, that the macrocycle L^3 folds to provide the same arrangement in the equatorial plane as found in the nickel(II) complexes of L^2. In this case, one apical ring must be six membered. As will be demonstrated below, the in-plane fields experienced by the nickel(II) ion in L^2 and in L^3 determined *via* analysis of the electronic spectrum are essentially identical, providing further evidence for equivalent in-plane structures. Table 1 includes thermodynamic data for some related nickel(II) complexes and a comparison of these data with those for nickel(II) complexes of L^1—L^3 is worthwhile.

The open-chain analogue of $[NiL^1]^{2+}$ is $[Ni(tetren)]^{2+}$, whose heat of formation is actually larger (see Table 1). Insofar as enthalpy is concerned, this could be construed to be a negative macrocyclic effect. However, $\Delta S^\ominus$ (not yet measured) for the macrocycle may favour $[NiL^1]^{2+}$ and lead to a higher value of log K. Alternatively (since the plane of the molecule is relatively open), these macrocycles may be viewed as extensions of open-chain tetra-amines. From the effect of the addition of one nitrogen atom [$-$(3—5) kcal mol^{-1}] to the $\Delta H^\ominus$ value for the appropriate linear tetra-amine $H_2N[CH_2]_2NH[CH_2]_2NH[CH_2]_2NH_2$ ($-\Delta H^\ominus$ = 14 kcal mol^{-1}) one can predict that $-\Delta H^\ominus$ = 17—19 kcal mol^{-1} for $[NiL^1]^{2+}$ or $[Ni(tetren)]^{2+}$. Indeed the prediction for $[Ni(tetren)]^{2+}$ is correct but overestimates the macrocyclic enthalpy. This 'negative macrocyclic enthalpy effect' almost certainly arises as a consequence of strain in the molecule.

There is no direct open-chain analogue of L^2. In the plane, we have the alternating ring sequence (2,3,2).* The heat of formation ($-\Delta H^\ominus$) of the nickel(II) complex of the linear tetra-amine $H_2N[CH_2]_2NH[CH_2]_3NH[CH_2]_2NH_2$ is 19.2 kcal mol^{-1}, to which can be added 3—5 kcal mol^{-1} to predict a $-\Delta H^\ominus$ for $[NiL^2]^{2+}$ of 22—24 kcal mol^{-1}. The observed value of 23.04 kcal mol^{-1} falls beautifully into this range. However, this would be the value predicted for an open-chain penta-amine with a single six-membered ring.

The replacement of an apical five-membered ring in $[NiL^2]^{2+}$ with a six-membered apical ring to form $[NiL^3]^{2+}$ causes a significant loss of exothermicity, to a value almost identical with that for the linear quadridentate amine $H_2N[CH_2]_2NH[CH_2]_3NH[CH_2]_2NH_2$. In comparison with the nickel complex of the latter, the addition of the fifth nitrogen atom seems athermic. Thus in none of these complexes is there a positive macrocyclic enthalpy effect.

We may tentatively ascribe its absence to the absence of a closed macrocyclic ring in the molecular plane; these species are more characteristic of open-chain amines. It is relevant that the nickel(II) complex of the fourteen-membered tetra-aza macrocycle, having the sequence (2,2,2,4), has the same exothermicity as that of the open-chain $H_2N[CH_2]_2NH[CH_2]_2NH[CH_2]_2NH_2$. Evidently, a seven membered ring (in 2,2,2,4) is large enough to remove the macrocyclic characteristic.[21]

Electronic Spectra.—The nickel(II) complexes of L^2 and L^3 have spectra very reminiscent of tetragonally distorted octahedra,[22] at least insofar as band energies are concerned (Table 2). Most significantly there are no low-lying bands below 10 000 cm^{-1} which would be indicative of seven-co-ordination in these systems.[23] The relative intensities are atypical in that the lowest-energy *d–d* transition (a component of $^3T_{2g}\leftarrow{}^3A_{2g}$ in O_h) is more intense than components of $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ (in O_h). Usually the reverse is true. It is interesting to note that this same reversal of relative intensities is seen in the open-chain $[Ni(tetren)(OH_2)]^{2+}$ species.[15] Aside from this, the spectra, at least of the nickel(II) complexes of L^2 and L^3, are very similar to those of tetra-

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* The numbers in parentheses indicate the numbers of C atoms in each ring in the metal complex. A two-carbon ring will be five membered, a three-carbon ring will be six membered.

gonal $[NiL_2X_2]$ species (L = *NN'*-dialkylethane-1,2-diamine, X = halide or carboxylate) [24] and significantly different, in band envelope, from nickel(II) complexes of L^5, L^3, and L^4 reported by Busch and co-workers.[25] Thus, even in their electronic spectra, these macrocycles (at least L^2 and L^3) behave more like open-chain amines.

The assignment of $[NiL^2]^{2+}$ to D_{4h} symmetry seems straightforward with four nitrogen atoms in the plane and one apical, DT being negative and ${}^3E_g < {}^3B_{2g}$. The first broad peak at 10 420 cm^{-1} is, therefore, assigned to ${}^3E_g{}^a \leftarrow {}^3B_{1g}$. The next two weak peaks, near 12 000—13 000 cm^{-1}, are assigned to ${}^3B_{2g} \leftarrow {}^3B_{1g}$ and ${}^1A_{1g} \leftarrow {}^3B_{1g}$. The spin-singlet should be narrower than the spin-triplet transition. In this case, extensive mixing *via* spin–orbit coupling has evidently occurred. The peak at 19 230 cm^{-1} is clearly ${}^3E_g{}^b \leftarrow {}^3E_{1g}$ and the ${}^3A_{2g} \leftarrow {}^3B_{2g}$ transition can be seen as a broad feature under the low-energy tail of the former transition, near 17 000 cm^{-1}. Finally, ${}^3E_g{}^c \leftarrow {}^3B_{1g}$ lies at 30 525 cm^{-1}. These data can be fitted to yield the parameters shown in Table 3. The spectrum of $[NiL^3]^{2+}$ can be analysed in analogous fashion (see Tables 2 and 3). These data show that the apical field strength (DQ_A) in $[NiL^3]^{2+}$ is greater than in the L^2 species. This is consistent with the diminished axial strain in the former complex due to the presence of the six-membered apical ring. The equatorial fields (DQ_E) of the two complexes are effectively identical according to electronic spectroscopy.

If we tentatively assume that the metal–ligand angles are all close to 90°, we can utilize the orbital angular-overlap model in the tetragonal field [26] to obtain values of the axial and equatorial σ bonding. This is also given in Table 3 and compared with values for tetra-aza macrocycles. We observe that the σ_N values are well within the range expected for an amine bound to nickel(II),[26] whilst the apical field, σ_Z, is also in the range anticipated (*i.e.* water plus amine, $\sigma_Z \approx 3\,000$ cm^{-1}) [26] with some evidence for steric hindrance in $[NiL^2]^{2+}$. It is interesting to note that the electronic characteristics of the nickel(II) complexes of the penta-aza macrocycles L^2 and L^3 are most similar to those of the 15-membered tetra-aza macrocycle L^8, with the in-plane ring sequence (2,3,3,3) and with amine–nickel binding significantly less than in the $[NiL^5]^{2+}$ (2,3,2,3) species.

The spectrum of $[NiL^1]^{2+}$ (Figure 1) is anomalous with respect to the splitting and relative intensities of the first set of *d–d* bands (near 900 nm). It is reminiscent of the highly rhombically distorted bis(*NN*-diethylethane-1,2-diamine)bis(trichloroacetato)nickel(II) where the degeneracy of the first orbital triplet (in O_h) is totally resolved.[27] It is evident from these data that $[NiL^1]^{2+}$ possesses a highly distorted octahedral structure arising presumably from the strain in the molecule. Whilst it is understandable why the distortion evident in the complex of L^1 contributes to the lowest $-\Delta H^\ominus$ value, the spectroscopic data do not shed any light on why $-\Delta H^\ominus$ for the L^2 complex is greater than for the L^3. The reverse order might have been anticipated based upon equivalent in-plane field strengths, and a greater apical field strength for the latter. We must await further thermodynamic data for penta-aza macrocycle complexes and perhaps single-crystal electronic spectroscopic data before further discussion becomes useful.

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